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(54) Title of the Invention

ALCOHOL FUEL CELL AND OPERATING METHOD THEREFOR

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## **SPECIFICATION**

### **1. Title of the Invention**

Alcohol Fuel Cell and Operating Method Therefor

### **2. Claims**

(1) In an alcohol fuel cell in which an air (oxygen) electrode 2 and a fuel electrode 3 are arranged opposite each other with an intervening cation exchange membrane 1, the alcohol fuel cell is characterized in that the above mentioned fuel electrode 3 comprises a catalyzer layer 18 with which the electrolyte is stored and a water repellent layer 17 with which the reaction product gas is exhausted, and the above mentioned catalyzer layer 18 is in contact with the cation exchange membrane 1 side, and the water repellent layer 17 is disposed on the aqueous alcohol fuel solution 7 side, and is equipped with an alcohol fuel container 8 that is connected through to a fuel electrode solution chamber 10 such that the above mentioned aqueous alcohol fuel solution 7 can circulate passing through an external flow path, and is configured such that the alcohol fuel circulates and is supplied to the fuel electrode solution chamber 10 of each cell by the ascending action of the bubble form reaction product gas 9.

(2) The alcohol fuel cell cited in Claim 1 in which, in the alcohol fuel container 8 that is connected through to the fuel electrode solution chamber 10 such that circulation is possible passing through an external flow path, the front opening, which is the exhaust orifice 11, is disposed in a location that is higher than the exhaust fluid surface 12 such that the above mentioned the product gas 9 that has reacted at the above mentioned fuel electrode 3 can easily ascend in the fuel electrode solution chamber 10.

(3) The alcohol fuel cell cited in Claim 1 that is furnished with a gas supply system 23 with which, together with the ascending action in the above mentioned fuel electrode solution chamber 10 of the gas 9 that has been produced in a reaction at the fuel electrode 3, a gas 24 is supplied in a bubble form into the fuel electrode solution chamber 10 from outside the fuel cell main body and the circulation of the aqueous alcohol fuel solution 7 is promoted.

(a) In an alcohol fuel cell in which an air (oxygen) electrode 2 and a fuel electrode 3 are arranged opposite each other with an intervening cation exchange membrane 1, the alcohol fuel cell is characterized in that the above mentioned fuel electrode 3 comprises a catalyzer layer 18 with which the electrolyte is stored and a water repellent layer 17 with which the reaction product gas 9 is exhausted, and the above mentioned catalyzer layer 18 is in contact with the cation exchange membrane 1 side, and the water repellent layer 17 is disposed on the aqueous alcohol fuel solution 7 side, and is equipped with an aqueous alcohol fuel solution container 8 that is connected through to a fuel electrode solution chamber 10 such that the above mentioned aqueous alcohol fuel solution 7 can circulate passing through an external flow path, and in addition, an aqueous alcohol fuel solution supply system 25 is disposed in series or in parallel between the alcohol fuel cell main body and the aqueous

alcohol fuel solution container 8, and is configured such that the alcohol fuel is supplied to the fuel electrode solution chamber 10 of each cell in a combined application with the forced circulation of the alcohol fuel.

(5) In an operating method for an alcohol fuel cell in which an air (oxygen) electrode 2 and a fuel electrode 3 are arranged opposite each other with an intervening cation exchange membrane 1, the operating method for the alcohol fuel cell is characterized in that the above mentioned fuel electrode 3 comprises a catalyzer layer 18 with which the electrolyte is stored and a water repellent layer 17 with which the reaction product gas is exhausted, and the above mentioned water repellent layer 17 is disposed on the aqueous alcohol fuel solution 7 side, and the reaction product gas passes through the water repellent layer 17 and is emitted as the bubble form 9 into the aqueous alcohol fuel solution 7, and the aqueous alcohol fuel solution 7 is circulated and is supplied to the fuel electrode solution chamber 10 of each cell by the ascending action of the bubble form reaction product gas 9.

(6) The operating method for an alcohol fuel cell cited in Claim 5 in which the ascending action in the fuel electrode solution chamber 10 of the gas 9 that has been produced by the reaction of the alcohol fuel at the fuel electrode 3 and the supply of the gas from outside the fuel cell main body in the bubble form 24, produces a combined application of the actions that promotes the circulation of the aqueous alcohol fuel solution 7, and the aqueous alcohol fuel solution is supplied to the fuel electrode solution chamber 10 of each fuel cell.

(7) In an operating method for an alcohol fuel cell in which an air (oxygen) electrode 2 and a fuel electrode 3 are arranged opposite each other with an intervening cation exchange membrane 1, the operating method for the alcohol fuel cell is characterized in that the above mentioned fuel electrode 3 comprises a catalyzer layer 18 with which the electrolyte is stored and a water repellent layer 17 with which the reaction product gas is exhausted, and the above mentioned water repellent layer 17 is disposed on the aqueous alcohol fuel solution 7 side, and the above mentioned reaction product gas passes through the water repellent layer 17 and is emitted in a bubble form into the aqueous alcohol fuel solution 7, and there is a combined application of the ascending action of the above mentioned reaction product gas in the fuel electrode solution chamber 10 and the circulating action of the aqueous alcohol fuel solution 7 in which the aqueous alcohol fuel solution supply system that is disposed in series or in parallel between the fuel cell main body and the aqueous alcohol fuel solution container 8 is operated continuously or intermittently and alcohol fuel is supplied to the fuel electrode solution chamber 10 of each cell.

### **3. Detailed Description of the Invention**

#### **Field of Industrial Utilization**

The present invention relates to an alcohol fuel cell with which alcohol is used as the liquid fuel and air and oxygen are made the oxidizing agents as well as the improvement of an operating method therefor.

#### **Prior Art**

For some time, for alcohol fuel cells, there have been alkali types in which an aqueous solution of caustic potash is used and acidic types in which an aqueous solution of sulfuric acid is used and there is much research of alcohol fuel cells in which the carbon dioxide gas, which is an alcohol fuel reaction product, does not react with the electrolyte. For the supply of the alcohol fuel to the acidic-type alcohol fuel cell, a fuel dissolved electrolyte (an anolyte) is circulated passing through each liquid chamber of the alcohol fuel cell. There is a circulation type fuel dissolved electrolyte format in which alcohol fuel is supplied from the alcohol fuel tank into the fuel dissolved electrolyte tank that is connected through to this in conformance with the amount consumed and the fuel dissolved electrolyte (the anolyte) is replenished into each liquid chamber of the alcohol fuel cell. There is also a static type fuel dissolved electrolyte format in which the alcohol fuel is supplied directly into each cell's liquid chamber in conformance with the amount consumed. Since an aqueous solution of sulfuric acid is used as the electrolyte in the former, in those cases where each cell has been laminated, a shunting of the liquid that passes through the fuel dissolved electrolyte supply path that is disposed on the bottom in each cell is produced and brings about a degradation of the performance of the fuel cell. In addition, the corrosiveness of the electrolyte is strong and there are many failures of the electrolyte circulation pump and there has been the issue that damage to the fuel cell is also great. Since, with the latter, each cell is assembled independently, it is possible to prevent the shunting phenomenon due to the electrolyte but the amount of alcohol fuel that is consumed by each cell is not the same and, in addition, supplying the alcohol fuel uniformly to each cell's liquid chamber is difficult and there has been the issue that the long term operation of the alcohol fuel cell in a stable state is not possible.

In order to resolve these issues and to further circulate the fuel dissolved electrolyte (the anolyte) in each cell by means of the lift effect of the gas produced at the fuel electrode, an alcohol fuel cell in which the fuel dissolved electrolyte (the anolyte) in each cell is made independent and shunting by the electrolyte is prevented has been proposed (Japanese Unexamined Patent Application Publication (Kokai) Number Sho 61-271753). In addition, there is also a proposal to provide a fuel dissolved electrolyte (an anolyte) reservoir, detecting the concentration of the fuel in the fuel dissolved electrolyte (the anolyte), supplying an appropriate amount of alcohol fuel to the fuel dissolved electrolyte (the anolyte), then sufficiently mixing and supplying this to each cell, but it is considered that complicated operation would be necessary (Japanese Unexamined Patent Application Publication (Kokai) Number Sho 62-229770).

#### Problems of Prior Art To Be Addressed by the Invention

With the configurations of the past, because the alcohol fuel dissolved electrolyte (the alcohol dissolved aqueous sulfuric acid solution) that is in the liquid chambers of each of the cells of the alcohol fuel cell is circulated by means of the reaction production gas, there are cases in which the aqueous sulfuric acid solution, which is highly corrosive, leaks out or scatters to the outside and there are problems such as those from the standpoint of safety and that other equipment is corroded. In addition, due to the relationship with the concentration (the specific gravity) of the aqueous sulfuric acid solution that is in each of the liquid chambers of the cells of the alcohol fuel cell, the ascending speed of the reaction product gas is not necessarily rapid and in those cases where a current density is produced, cells in which there is an insufficient supply of the alcohol fuel arise and the life of the fuel cell is shortened.

On the other hand, in order to supply the electrolyte in which the alcohol fuel has been dissolved such that the fuel contacts the catalyst of the fuel electrode in the fuel cell's liquid chamber, the alcohol fuel also comes into contact with the air (oxygen) electrode and there is an action that tends to lower the potential of the air (oxygen) electrode. The greater this amount becomes, the lower the performance of the air (oxygen) electrode. Accordingly, the extraordinarily accurate control of the alcohol fuel concentration is necessary and this leads to such problems as increased cost for the addition of a complicated alcohol fuel supply system.

Therefore, focusing on circulating by means of the reaction product gas only a non-corrosive and highly safe aqueous alcohol fuel solution, the object is to make the structure of the fuel electrode 3 a two-layer one with a catalyzer layer and a water repellent layer, have the reaction product gas emitted from the water repellent layer side and make a configuration in which the alcohol fuel flows and circulates in each fuel cell's liquid chamber of the fuel cell due to the ascending action of the reaction product gas. In addition, in order to further promote the ascending action of the reaction product gas, establish in parallel both a gas supply system and an aqueous alcohol fuel solution supply system as a supplemental means and obtain an alcohol fuel cell that has superior characteristics operated continuously or intermittently and that is, moreover, highly safe as well as an operating method for it.

#### Measures To Solve the Problems of Prior Art

In order to resolve these issues, the present invention is one with which in an alcohol fuel cell in which an air (oxygen) electrode 2 and a fuel electrode 3 are arranged opposite each other with an intervening cation exchange membrane 1, a configuration in which the above mentioned fuel electrode 3 comprises a catalyzer layer 18 with which the electrolyte is stored and a water repellent layer 17 with which the reaction product gas is exhausted, and the catalyzer layer 18 is in contact with the cation exchange membrane 1 side, and the water repellent layer 17 is disposed on the aqueous alcohol fuel solution 7 side, and is equipped with an alcohol fuel container 8 that is connected through to a fuel electrode solution chamber 10 such that the above mentioned aqueous alcohol fuel solution 7 can circulate passing through an external flow path (the direction of the arrows), such that the alcohol fuel circulates to the fuel electrode solution chamber 10 of each cell by the ascending action of the reaction product gas 9, as well as an operating method therefor are obtained.

Associated with this, the front opening, which is the exhaust orifice 11, is disposed in a location that is higher than the exhaust fluid surface 12 such that the product gas 9 that has reacted at the above mentioned fuel electrode 3 can easily ascend in the fuel electrode solution chamber 10. Moreover, the invention is one with which a configuration that is furnished with a gas supply system 23 having an action with which the circulation of aqueous alcohol fuel solution 7 is promoted and an operating method therefor are obtained.

As the next invention, the invention is one with which a configuration that is furnished with an aqueous alcohol fuel solution supply system 24 that is in series or in parallel between the alcohol fuel cell main body and the aqueous alcohol fuel solution container 8 and with which there is a combined application of a forced circulation action for the alcohol fuel in addition to the ascending action of the reaction

product gas in the above mentioned fuel electrode solution chamber 10 and an operating method therefor are obtained.

#### Action

By means of this kind of configuration and operating method, since only the aqueous alcohol fuel solution that does not include the electrolyte is circulated and supplied to the fuel electrode in the liquid chamber, even if, for a time, there is leakage to the outside, there is no damage done to the peripheral equipment (corrosion due to the electrolyte) and safety during operation is extraordinarily high.

In addition, since the specific gravity of the aqueous alcohol fuel solution is lower than that of the acidic electrolyte (the anolyte), the effect of the ascending action of the reaction product gas is great and the alcohol fuel is supplied in compliance with the load and with a uniform distribution.

With regard to the fuel electrode, because there is no need to strictly control the alcohol concentration since the alcohol fuel is supplied to the water repellent layer side of the fuel electrode, the adjustment of the fuel concentration is extraordinarily simple. In particular, in those cases where a high load is established, by means of the arrangement of an air pump or a liquid supply pump and the like as a means to assist the alcohol fuel supply, the invention possesses an action that progresses with good efficiency. Since the alcohol is supplied uniformly in each cell even under high loads, in those cases where the fuel cell has been laminated, there is an action that extends the cell characteristics and the cell life.

Since a supplemental system is used in parallel with the natural circulation supply format and operated continuously or intermittently, the power consumption of the supplemental equipment is low and the amount of fuel consumed is reduced, and together with this, it is possible to improve the cell characteristics and reliability.

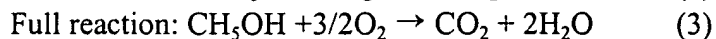
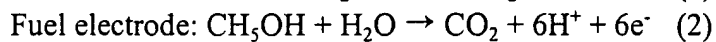
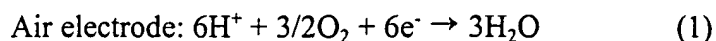
#### Preferred Embodiments of the Invention

A further detailed explanation will be given below by means of preferred embodiments.

##### Preferred Embodiment 1

As one example, the fuel electrode and the air electrode that comprise the alcohol fuel cell were produced while referring to Japanese Examined Patent Application Publication (Kokoku) Number Sho 63-115794. The configuration of the alcohol fuel cell in which the air electrode and the fuel electrode have been used with an intervening cation exchange membrane (a Nafion membrane manufactured by Dupont) is shown in Fig. 1. In addition, an expanded structural portion of the fuel cell is shown in Fig. 2. In Fig. 1, the air electrode 2 and the fuel electrode 3 are disposed with the cation exchange membrane 1 interposed between them, the air, which is the oxidizer, enters through the air supply orifice 4, passes through the gas chamber 5, and is exhausted through the air exhaust orifice 6. On the other hand, the alcohol fuel, which is the reducing agent, is mixed with water, and stored in the aqueous

alcohol fuel solution container 8 as the aqueous alcohol fuel solution 7. The alcohol fuel is reacted, the gas 9 (primarily carbon dioxide gas) that has been produced ascends in the fuel electrode solution chamber 10, and is exhausted from the exhaust orifice 11 of the fuel electrode solution chamber 10 together with the aqueous alcohol fuel solution 7. The front opening, which is the exhaust orifice 11, is disposed above the exhaust fluid surface 12 such that the reaction product gas 9 can easily ascend in the fuel electrode solution chamber 10. The aqueous alcohol fuel solution that has come out from the exhaust orifice is once more recirculated to the aqueous alcohol fuel solution container 8. The alcohol fuel is replenished from the fuel solution fill orifice 13 in conformance with the amount that has been consumed. The air electrode 2 is attached to the positive terminal 14 and the fuel electrode 3 is attached to the negative terminal 15. Next, as is shown in Fig. 2, in the air electrode 2, the platinum catalyst carrier carbon material with the interposed conductive porous substrate (carbon paper) 16 is comprised, the fuel electrode 3 comprises the water repellent layer 17 and the catalyzer layer 18, and in the catalyzer layer 18, the carbon material with which the platinum-ruthenium catalyst is comprised, and is in close contact with the cation exchange membrane 1 side. The water repellent layer 17 of the fuel electrode 3 is disposed on the aqueous alcohol fuel solution 7 side. By means of this kind of configuration, while the alcohol fuel is circulated in the direction of the arrows between both, in the aqueous alcohol fuel solution container 8 that is connected through to the fuel electrode solution chamber 10 of the alcohol fuel cell, the alcohol fuel and the oxygen (the air) in the gas chamber 6 cause an electrochemical reaction and it is possible to generate electricity in accordance with the following reaction formulas. Methanol is used as the alcohol fuel in the present invention.



As can be understood from formulas (2) and (3), the carbon dioxide gas, which is a reaction product, passes through the water repellent layer 17 of the fuel electrode 13 [sic], becomes the bubble form 9, and is emitted into the aqueous alcohol fuel solution 7. When the bubble form 9 carbon dioxide gas ascends, the alcohol fuel also moves and it is possible to circulate the alcohol fuel in conformance with the load. In particular, since this is in an aqueous alcohol fuel solution that has a low specific gravity, the distribution is uniform in the fuel electrode solution chamber 10 and, moreover, circulation with a high ascending speed is possible.

## Preferred Embodiment 2

A conceptual drawing of an alcohol fuel cell of a laminated type structure having a configuration in which an air electrode 2 and a fuel electrode 3 in accordance with the same production method as in Preferred Embodiment 1 are used with a cation exchange membrane 1 (a Nafion membrane manufactured by Dupont) interposed between the two electrodes is shown in Fig. 3. An expanded structural portion of the laminated cell is shown in Fig. 4. In Fig. 3, the aqueous alcohol fuel solution container 8 that stores the aqueous alcohol fuel solution 7 containing the alcohol fuel, which is a reducing agent, is connected through to the fuel electrode solution chamber 10 of each cell of the laminated fuel cell main body 19 via an aqueous alcohol fuel solution distribution orifice 20 and an



exhaust orifice 11. The front opening, which is the exhaust orifice 11 of each cell, is disposed above the exhaust fluid surface 12 such that the alcohol fuel easily passes through and is circulated through the fuel electrode solution chamber 10 of each cell due to the ascending action of the reaction product gas 9. The aqueous alcohol fuel solution 7 that comes out from the exhaust orifice 11 is recirculated once again to the aqueous alcohol fuel solution container 8. The alcohol fuel is replenished from the fuel solution fill orifice 13 in conformance with the amount that has been consumed. The alcohol fuel cell has been configured such that the air, which is an oxidizer, is supplied from the fuel cell side window and exhausted from the side window on the opposite side and the top surface window. Next, as is shown in Fig. 4, the cell is configured as a single unit with the air electrode 2, the cation exchange membrane 1, the fuel electrode 3, the solution chamber 10, the separation plate 21, the gas (air) chamber 5, the air electrode 2, and the cation exchange membrane 1 in order from the left. By means of this kind of configuration, while the alcohol fuel in the aqueous alcohol fuel solution container 8 (for example, a "U" shaped container) that is connected through to the fuel electrode solution chamber 10 of each cell of the laminated type alcohol fuel cell is circulated between both in the direction of the arrows, an electrochemical reaction of the alcohol fuel and the air (the oxygen) is brought about and it is possible to impose a load continuously.

### Preferred Embodiment 3

A laminated type alcohol fuel cell having a configuration in which an air electrode 2 and a fuel electrode 3 in accordance with the same production method as in Preferred Embodiment 1 are used with a cation exchange membrane 1 (a Nafion membrane manufactured by Dupont) interposed between the two electrodes is shown in Fig. 5. In accordance with Fig. 5, this is a configuration and an operating method with which the branching tube 22 having a bubble supply orifice is disposed in the vicinity of the bottom section of the "U" type aqueous alcohol fuel solution container 8 facing toward the fuel electrode solution chamber 10 in order to supply the bubbles 24 to the fuel electrode solution chamber 10 of each of the cells of the alcohol fuel cell by means of the operation of the gas supply system (an air supply pump) 23 that are used in parallel with the bubbles 9, which are the reaction product gas, to supply the aqueous alcohol fuel solution 7 to the fuel electrode solution chamber 10 of each of the cells. Other than this configuration and operating method, the cell is made completely with the same configuration as that of preferred embodiment 2.

### Preferred Embodiment 4

A laminated type alcohol fuel cell having a configuration in which an air electrode 2 and a fuel electrode 3 in accordance with the same production method as in Preferred Embodiment 1 are used with a cation exchange membrane 1 (a Nafion membrane manufactured by Dupont) interposed between the two electrodes is shown in Fig. 6. In accordance with Fig. 6, the aqueous alcohol fuel solution supply system 25 (a liquid pump) is disposed in the vicinity of the lower portion of the "U" type aqueous alcohol fuel solution container 8 in series between the container that is divided in two. This is a configuration and an operating method with which, by means of this structure, due to the combined application of the ascending action of the bubbles 9, which are the reaction product gas, of the fuel electrode solution chamber 10 and the aqueous alcohol fuel solution 7 circulating action from the

operation of the liquid pump 25, the aqueous alcohol fuel solution 7 is supplied to the fuel electrode solution chamber 10 of each cell. Other than this configuration and operating method, the cell is made completely with the same configuration as that of preferred embodiment 2.

#### Preferred Embodiment 5

A laminated type alcohol fuel cell having a configuration in which an air electrode 2 and a fuel electrode 3 in accordance with the same production method as in Preferred Embodiment 1 are used with a cation exchange membrane 1 (a Nafion membrane manufactured by Dupont) interposed between the two electrodes is shown in Fig. 7. In accordance with Fig. 7, the aqueous alcohol fuel solution supply pump 25, which is a joint supply system in parallel with the aqueous alcohol fuel solution 7 flow path in the container that is divided in two, is disposed in the vicinity of the lower section of the aqueous alcohol fuel solution container 8.

This is a configuration and an operating method with which, by means of this structure, due to the combined or independent application of the ascending action of the bubbles 9, which are the reaction product gas, of the fuel electrode solution chamber 10 and the aqueous alcohol fuel solution 7 circulating action from the operation of the aqueous alcohol fuel solution supply pump 25, the aqueous alcohol fuel solution 7 is supplied to the fuel electrode solution chamber 10 of each cell.

In particular, in those cases where a large load is placed on the fuel cell, there is a combined application of the aqueous alcohol fuel solution supply pump 25 operation and the amount of alcohol fuel supplied is increased. When the load is small, the operation of the aqueous alcohol fuel solution supply pump 25 is halted and power consumption other than that of the load is reduced. Instead of the aqueous alcohol fuel solution supply pump 25, the same effect may be obtained with a system such as the vane type rotating drive system 25' like that shown in Fig. 8. Other than this configuration and operating method, the cell is made completely with the same configuration as that of preferred embodiment 2.

A "U" type aqueous alcohol fuel solution container such as that cited in the drawings is used for preferred embodiments 2 through 5 but, in short, one with a structure with which the circulation of the alcohol fuel in the fuel electrode solution chamber of the alcohol fuel cell is facilitated is desirable. The flow path for the alcohol fuel that is supplied from the bottom of the fuel electrode solution chamber 10 may also be in the main body of the fuel cell. In other words, it may also be a branching aqueous alcohol fuel solution distribution tube.

#### Comparative Example

A conventional type fuel cell is shown in Fig. 9 as a comparative example. A cross-section along a-a' of Fig. 9 is shown in Fig. 10. In Fig. 9, the anolyte flow paths 29 and 29' are disposed between the fuel cell main body 27 and the barrier walls 28 and 28'; the anolyte flows in the direction of the arrows from the bottom surface section of the cell frame 30 and is exhausted from the anolyte exhaust hole 31. The exhaust hole 31 is disposed in a location that is higher than the anolyte solution surface and the alcohol fuel is supplied to the alcohol fuel cell solution chamber from the fuel supply paths 33 and 33'. The cell

is configured such that the alcohol fuel is supplied to the fuel electrode while the anolyte is circulated in the direction of the arrows.

In Fig. 10, the configuration in the cell frame comprises the solution chamber 34, the fuel electrode 35, the cation exchange membrane 36, and the air electrode 37. The fuel electrode has a structure in which the platinum catalyst is carried by carbon powder and the air electrode is a mixture of carbon powder, which carries the platinum catalyst and a water repellent agent, and these are formed into single units with the application of pressure.

The characteristics of the alcohol fuel cell in accordance with the configuration and operating method of this working example is shown in Table 1. A 3 M concentration aqueous methanol solution was used and 1.5 M sulfuric acid was impregnated on the catalyzer layer as the measured conditions. The measured temperature was 60 °C and the amount of air was made five times or more than the theoretical value. For the comparative example, a 3 M concentration solution of sulfuric acid for a methanol concentration of methanol (an anolyte) was used and all the other conditions were made the same as those of preferred embodiments 1 through 5. The terminal voltages for each current density were compared for the preferred embodiments and the conventional example.

	30 mA/cm <sup>2</sup>	60 mA/cm <sup>2</sup>	100 mA/cm <sup>2</sup>
Preferred embodiment 1	0.57 V	0.40 V	0.34 V
Preferred embodiment 2	0.55 V	0.395 V	0.33 V
Preferred embodiment 3	0.55 V	0.39 V	0.35 V
Preferred embodiment 4	0.56 V	0.41 V	0.365 V
Preferred embodiment 5	0.56 V	0.41 V	0.365 V
Comparative example	0.54 V	0.38 V	0.30 V

With the operation of the fuel cell of the present invention, in preferred embodiments 1 through 5, the mean cell voltage for each current was 0.55 to 0.57 V for a current density of 30 mA/cm<sup>2</sup>, 0.39 to 0.41 V for a current density of 60 mA/cm<sup>2</sup>, and 0.33 to 0.365 V for a current density of 100 mA/cm<sup>2</sup> and for the voltage difference, there was a gradual increase of 0.02 V, 0.03 V, and 0.035 V respectively. A large difference was not ascertained. In contrast to this, with the fuel cell of the past in the comparative example, the voltage was 0.01 V to 0.03 V for a current density of 30 mA/cm<sup>2</sup>, 0.01 to 0.03 V for a current density of 60 mA/cm<sup>2</sup>, and 0.03 to 0.065 V for a current density of 100 mA/cm<sup>2</sup> and the voltage is low compared to the fuel cell of the present invention. In particular, the higher the current

density becomes, the greater is that tendency exhibited. Even compared to the fuel cell of preferred embodiment 2, a higher voltage of from 0.01 to 0.03 V is exhibited depending on the current density. It is thought that the reason for this is that, due to the fact that there is a difference in specific gravity of the electrolyte and water, the buoyancy of the reaction product gas (the carbon dioxide gas) apparently works to lift the water, which has a lower specific gravity, more and, in order to make the circulation of the alcohol fuel faster, the potential of the fuel electrode is increased and a difference in the cell voltage becomes manifest. That tendency/becomes especially strong when the current density is high.

Among these preferred embodiments also, even when a single cell and a laminated cell are compared, since the conductivity of the aqueous alcohol fuel solution is lower than the conductivity of the anolyte, the cell voltage due to the solution shunting is extraordinarily slight. This fact can be understood well when looking at preferred embodiment 1 and preferred embodiment 2. Accordingly, by means of the lamination, the self power consumption is extremely small and the advantages from a practical standpoint are great. With this laminated type fuel cell, a large voltage difference is not observed at a low current density but when the current density becomes high, the circulation of the alcohol fuel using only the ascending action of the reaction product gas becomes insufficient. In other words, the supply of the alcohol fuel to the fuel electrode in conformance with the load is deficient. Therefore, when bubbles are sufficiently supplied by the air pump in the solution chamber 8 of the fuel electrode in order to eliminate this phenomenon, the circulation of the aqueous alcohol fuel solution is facilitated and an increase of the fuel cell voltage is observed. In addition, when the circulation of the aqueous alcohol fuel solution is carried out supplementarily with an aqueous alcohol fuel solution supply pump, the voltage of the fuel cell at a high current density is increased. By means of the supplemental use of an air supply pump or an aqueous alcohol fuel solution supply pump and the like in conformance with the load, the fuel cell is not damaged and it is possible to obtain a long lived and high performance fuel cell. Continuously or intermittently carrying out the operation of the air supply pump and the aqueous alcohol fuel solution supply pump as required, it is possible to reduce the power consumption of the supplemental system and to raise the electric generating efficiency of the alcohol fuel cell system.

In addition, since the fuel cell of the present invention circulates alcohol (methanol) and water, even if there is leakage of the solution for a time to the outside, there is no damage to the equipment. However, with a fuel cell of the past, since sulfuric acid is used in the anolyte, the damage to the equipment is great and the fuel cell of the present invention is also superior from the standpoint of the corrosive properties.

In these preferred embodiments, an air supply pump is used as the gas supply system but if it is a compressed gas or other gas generating system, the same effect can be obtained with any of them. In addition, an aqueous alcohol fuel solution supply pump is used as the aqueous alcohol fuel solution supply system but any generally used liquid supply system may be employed. In these preferred embodiments, air is used as the oxidizer but although, when an oxidizing gas is used, the economic properties are degraded, an alcohol fuel cell of increased performance can be obtained.

Methanol is used as the reducing agent but other alcohols such as ethanol and the like may also be used. However, methanol has the most superior characteristics.

It is configured such that the air, which is the oxidizer, is supplied from the side of the fuel cell and is exhausted from the opposite side or the top, however, it may be configured such that the air may be supplied from the bottom of the fuel cell and exhausted from the top. In addition, due to the fact that the front opening, which is the aqueous alcohol fuel solution exhaust orifice, is disposed above the exhaust fluid surface, the aqueous alcohol fuel solution in the fuel electrode solution chamber is more easily circulated with good efficiency. The state in which the bubbles collect in the fuel electrode solution chamber and the alcohol fuel distribution becomes non-uniform is eliminated. Accordingly, since the alcohol fuel is distributed uniformly, the life of the fuel cell is increased and its reliability is also superior.

#### **Advantageous Result of the Invention**

As described above, in accordance with the present invention, the advantageous result is obtained that it is possible to present an alcohol fuel cell and an operating method therefor with which, since the aqueous alcohol fuel solution is circulated, safety is high, a high voltage can be maintained even at a high current density, power consumption by auxiliary equipment is low, and there is little degradation of the cell performance at a high degree of efficiency even with long term power generation.

#### **4. Brief Description of the Drawings**

Fig. 1 depicts the configuration of an alcohol fuel cell;

Fig. 2 depicts an expanded view of a portion of the fuel electrode of Fig. 1;

Fig. 3 depicts the laminated structure of an alcohol fuel cell;

Fig. 4 depicts an expanded view of a portion of a laminated fuel cell;

Fig. 5 depicts the structure of a laminated type alcohol fuel cell that has been furnished with a gas supply system;

Fig. 6 depicts the structure of a laminated type alcohol fuel cell that has been furnished with an aqueous alcohol fuel solution supply pump;

Fig. 7 depicts the structure of a laminated type alcohol fuel cell that has been furnished with an aqueous alcohol fuel solution supply pump in parallel with the flow path;

Fig. 8 depicts another example of an aqueous alcohol fuel solution supply system;

Fig. 9 depicts the structure of an alcohol fuel cell of the past; and

Fig. 10 is a cross-section drawing along a-a' of Fig. 9.

#### **Reference Characters**

- 1: cation exchange membrane
- 3: fuel electrode
- 7: aqueous alcohol fuel solution
- 8: aqueous alcohol fuel solution container
- 9: reaction product gas (bubble form)
- 10: fuel electrode solution chamber
- 11: exhaust orifice /
- 12: exhaust fluid surface
- 17: water repellent layer
- 18: catalyzer layer
- 22: branching tube
- 23: air supply pump
- 24: bubbles that are supplied by the air supply pump
- 25: aqueous alcohol fuel solution supply pump
- 26: aqueous alcohol fuel solution flow path

Agent: Shigetaka Kurino, patent attorney (and one other)

Fig. 1

- 1: cation exchange membrane
  - 2: air electrode
  - 3: fuel electrode
  - 4: air supply orifice
  - 5: gas chamber
  - 6: air exhaust orifice
  - 7: aqueous alcohol fuel solution
  - 8: aqueous alcohol fuel solution container
  - 9: reaction product gas
  - 10: fuel electrode solution chamber
  - 11: aqueous alcohol fuel solution exhaust orifice
  - 12: exhaust fluid surface
  - 13: alcohol fuel fill orifice
  - 14: positive terminal
  - 15: negative terminal
- [arrow above 4] air

Fig. 2

- 16: conductive porous substrate
- 17: water repellent layer
- 18: catalyzer layer

Fig. 3

- 20: aqueous alcohol fuel solution distribution orifice

[right side arrows] air

Fig. 4

21: separation plate

Fig. 5

22: branching tube /

23: air supply system

24: bubbles

[arrow above 23] air

Fig. 6

25: aqueous alcohol fuel solution supply system

Fig. 7

26: aqueous alcohol fuel solution flow path

Fig. 8

25': vane type rotating drive system

## PATENT ABSTRACTS OF JAPAN

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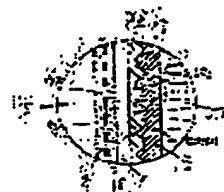
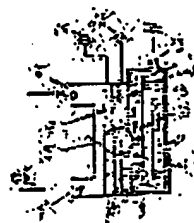
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## (54) ALCOHOLIC FUEL BATTERY AND OPERATING METHOD THEREOF

## (57)Abstract:

**PURPOSE:** To improve the safety and maintain the high voltage even at the high current density and reduce the demand of the auxiliary machine and reduce the lower of the battery performance at the time of generating electricity for a long time with the high efficiency by forming a fuel electrode with a catalyzer layer for storing the electrolyte and a water repellent layer for exhausting the reaction product gas, and circulating the alcoholic fuel aqueous solution.

**CONSTITUTION:** A fuel electrode 3 consists of a catalyzer layer 18 for storing the electrolyte and a water repellent layer 17 for exhausting the reaction product gas, and the catalyzer layer 18 contacts to the cation exchange membrane 1 side the water repellent layer 17 is located at the alcoholic fuel aqueous solution 7 side. The fuel electrode also comprise an alcoholic fuel aqueous container 8 for communicating a fuel electrode solution chamber 10 and an external passage so that the alcoholic fuel aqueous solution can circulate through them, and is formed so that the alcoholic fuel is circulated through the fuel electrode solution chamber 8 of each cell by the ascending work of the reaction product gas 9. Thereby, since the alcoholic fuel aqueous solution 7 which does not include the electrolyte is circulated to be supplied into the solution chamber 10 of the fuel electrode 3, even if the liquid spill to the outside is generated, the peripheral equipment is not damaged, and safety during the operation is sharply improved.



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⑭ 発明の名称 アルコール燃料電池及びその作動方法

⑰ 特 願 昭63-302887

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## 明 細 書

## 1. 発明の名称

アルコール燃料電池及び作動方法

## 2. 特許請求の範囲

(1) 陽イオン交換膜1を介して空気(酸素)極2と燃料極3を対向配置したアルコール燃料電池であって、上記燃料極3は電解質を貯蔵する触媒層18と反応生成ガスを排出する撥水層17とからなり、上記触媒層18は陽イオン交換膜1側に接し、撥水層17はアルコール燃料水溶液7側に配置され、上記アルコール燃料水溶液7が燃料極液室10と外部流路を通過して循環できるように連通するアルコール燃料容器8を具備し、気泡状反応生成ガス9の上昇作用によってアルコール燃料を各単電池の燃料極液室10内を通して循環供給する様に構成した事を特徴とするアルコール燃料電池。

(2) 燃料極液室10と外部流路を通過して循環できるように連通するアルコール燃料容器8において、上記燃料極3で反応した生成ガス9が燃料

極液室10内を上昇しやすいようにアルコール燃料水溶液7の排出口11である先端開口部が排出液面12よりも上部に配置されている特許請求の範囲第1項記載のアルコール燃料電池。

(3) 燃料極3で反応生成したガス9の上記燃料極液室10内での上昇作用と併せて燃料電池本体外部より気体24を燃料極液室10内に気泡状頭で供給し、アルコール燃料水溶液7の循環を助長する気体供給装置23を備えている特許請求の範囲第1項記載のアルコール燃料電池。

(4) 陽イオン交換膜1を介して空気(酸素)極2と燃料極3を対向配置したアルコール燃料電池であって、上記燃料極3は電解質を貯蔵する触媒層18と反応生成ガス9を排出する撥水層17とからなり、上記触媒層18は陽イオン交換膜1側に接し、撥水層17はアルコール燃料水溶液7側に配置され、アルコール燃料水溶液7が燃料極液室10と外部流路を通過して循環できるように連通するアルコール燃料水溶液容器8を備え、さらにアルコール燃料電池本体とア

アルコール燃料水溶液容器8との間に直列あるいは並列にアルコール燃料水溶液供給装置26を設け、アルコール燃料の強制循環作用を併用してアルコール燃料を各単電池燃料極液室10内に供給するよう構成した事を特徴とするアルコール燃料電池。

- (6) 陽イオン交換膜1を介して空気(酸素)極2と燃料極3を対向配置したアルコール燃料電池の作動方法であって、上記燃料極3は電解質を貯蔵する触媒層18と反応生成ガスを排出する撥水層17とからなり、上記撥水層17はアルコール燃料水溶液7側にあり、反応生成ガスは撥水層17を通してアルコール燃料水溶液7内に気泡状9で放出され、この気泡状反応生成ガス9の上昇作用によって、アルコール燃料水溶液7を循環させて各単電池燃料極液室10内にアルコール燃料を供給する事を特徴とするアルコール燃料電池の作動方法。
- (6) 燃料極3でアルコール燃料の反応によって生成したガス9の燃料極液室10内で上昇する作

10内に供給する事を特徴とするアルコール燃料電池の作動方法。

### 3. 発明の詳細な説明

#### 産業上の利用分野

本発明は液体燃料としてアルコールを用い、空気、酸素を酸化剤とするアルコール燃料電池及びその作動方法の改良に関するものである。

#### 従来の技術

従来、アルコール燃料電池には電解液として力性カリ水溶液を用いるアルカリ型と、硫酸水溶液を用いる酸性型とがあるが、アルコール燃料の反応生成物である炭酸ガスが電解液と反応しない酸性型アルコール燃料電池が多く研究されている。この酸性型アルコール燃料電池へのアルコール燃料の供給には燃料溶解電解液(アノライト)をアルコール燃料電池の各液室内を通して循環させ、これと連通する燃料溶解電解液タンク内にはアルコール燃料タンクより消費量に応じてアルコール燃料を供給する燃料溶解電解液循環型方式と燃料溶解電解液(アノライト)をアルコール燃料電池

用と、燃料電池本体外部より気体を燃料極液室10内に気泡状態24で供給し、アルコール燃料水溶液7の循環を助長する作用とを併用して、各単電池の燃料極液室10内にアルコール燃料水溶液を供給する特許請求の範囲第6項記載のアルコール燃料電池の作動方法。

- (7) 陽イオン交換膜1を介して空気(酸素)極2と燃料極3を対向配置したアルコール燃料電池の作動方法であって、上記燃料極3は電解質を貯蔵する触媒層18と反応生成ガスを排出する撥水層17とからなり、上記撥水層17はアルコール燃料水溶液7側にあり、上記反応生成ガスは撥水層17を通してアルコール燃料水溶液7内に気泡状態で放出され、燃料極液室10内における上記反応生成ガス9の上昇作用と、燃料電池本体とアルコール燃料水溶液容器8間に直列あるいは並列に配置されたアルコール燃料水溶液供給装置を連続的あるいは間欠的に動作させるアルコール燃料水溶液7の循環作用とを併用してアルコール燃料を各単電池燃料極液室

の各液室内に充填させ、消費量に応じてアルコール燃料タンクよりアルコール燃料を各単電池液室内に直接供給する燃料溶解電解液静止型方式とがある。前者は電解液として硫酸水溶液を用いるため、各単電池を積層した場合、各単電池内下部に設けてある燃料溶解電解液の供給通路を通しての液短絡が発生し、燃料電池の性能低下を引起す。また電解液の腐食性が強く電解液循環ポンプの故障が多く、燃料電池への損傷も大きいという課題があった。後者は各単電池を独立に組立てているために、電解液による短絡現象は防止できるが、各単電池のアルコール燃料消費量が同じでなく、また均一にアルコール燃料を各単電池液室内に供給する事が困難であり、アルコール燃料電池を安定した状態で、長時間作動させる事が出来ないという課題があった。

この課題を解決するために、さらに燃料極における生成ガスのリフト効果により各単電池毎に燃料溶解電解液(アノライト)を循環させ、アルコール燃料電池が各単電池毎に燃料溶解電解液(ア

ノライト)が独立し、電解液による短絡を防止する事が提案されている(特開昭61-271753号公報)。また燃料電池内に燃料溶解電解液(アノライト)溜を設け、この燃料溶解電解液(アノライト)中の燃料濃度を検出してアルコール燃料を適量燃料溶解電解液(アノライト)中に供給し、さらに十分攪拌し各単電池内に供給すると云う提案もあるが、複雑な操作が必要と考えられる(特開昭62-229770号公報)。

発明が解決しようとする課題

この様な従来の構成ではアルコール燃料電池の各単電池液室内にあるアルコール燃料溶解電解液(アルコール溶解硫酸水溶液)を反応生成ガスによって循環させるために腐食性の強い硫酸水溶液が外部に漏出・飛散する場合があります、安全性の点及び他の機器を腐食させる事などが課題となる。また、アルコール燃料電池の各単電池液室内にある硫酸水溶液の濃度(比重)の関係から反応生成ガスの上昇速度が必ずしも早くなく、高い電流密度を取り出す場合にはアルコール燃料の供給不足

併設し、連続的あるいは間欠的に動作させて特性の優れたしかも安全性の高いアルコール燃料電池及び作動方法を得ることを目的とするものである。

課題を解決するための手段

この課題を解決するために、本発明は陽イオン交換膜1を介して空気(酸素)極2と燃料極3を対向配置したアルコール燃料電池において、上記燃料極3は電解質を貯蔵する触媒層18と反応生成ガスを排出する撥水層17とからなり、触媒層18は陽イオン交換膜1側に接し、撥水層17はアルコール燃料水溶液7側に配置され、上記アルコール燃料水溶液7が燃料極液室10と外部流路(矢印方向)を通して循環できるように連通するアルコール燃料水溶液容器8を備え、反応生成ガス9の上昇作用によってアルコール燃料を各単電池の燃料極液室8内を通して循環させる構成とその作動方法を得るものである。

これに付随して上記燃料極3で反応した生成ガス9が燃料極液室10内を上昇しやすい様にアルコール燃料水溶液7の排出口11である先端開口

を起こす単電池が発生し、燃料電池の寿命を短縮する。

一方、アルコール燃料を溶解した電解液を燃料電池液室内の燃料極の触媒に接触する様に供給するために、アルコール燃料が空気(酸素)極にも接触し、空気(酸素)極の電位を下げる方向に作用し、その量が多くなればなる程空気(酸素)極の性能は低下する。したがって、非常に正確なアルコール燃料濃度の制御が必要となり、複雑なアルコール燃料の供給システムが付加されコストアップにつながるなどの課題も有している。

そこで、腐食性のない、安全性の高いアルコール燃料水溶液のみを反応生成ガスによって循環させる事に着目し、燃料極3の構成を触媒層と撥水層の2層とし、反応生成ガスを撥水層側より放出させ、この反応生成ガスの上昇作用によって、アルコール燃料が燃料電池の各燃料極液室内を流れて循環する構成とし、さらにこの反応生成ガスの上昇作用をより促進するための補助手段として、気体供給装置、アルコール燃料水溶液供給装置を

部が排出液面12より上部に配置され、しかもアルコール燃料水溶液7の循環を補助する作用を有する気体供給装置23を備える構成と、その作動方法を得るものである。

つぎの発明として、上記燃料極液室10内での反応生成ガス9の上昇作用とさらにアルコール燃料電池本体とアルコール燃料水溶液容器8間で直列あるいは並列にアルコール燃料水溶液供給装置24を備え、アルコール燃料の強制循環作用を併用した構成と、その作動方法を得るものである。

作 用

このような構成および作動方法により、電解液を含まないアルコール燃料水溶液のみを燃料極の液室内に循環供給させるため、仮に外部に液漏れしても周辺機器の損傷(電解液による腐食)がなく、作動中の安全性が非常に高くなる。

また、アルコール燃料水溶液の比重が酸性電解液(アノライト)より小さいため、反応生成ガスの上昇作用の効果が大きく、負荷に追従して均一な分布でアルコール燃料が供給される。

燃料極では燃料極の撥水層側にアルコール燃料を供給するために、アルコール濃度をきびしく規制する必要がないので、燃料濃度の調整が非常に容易となる。とくに高負荷を取り出す場合はアルコール燃料供給の補助手段として空気ポンプ、液体供給ポンプなどを配置する事によりアルコール燃料の供給をより効率よく進行させる作用を持っている。高負荷でも各単電池の中に均一にアルコール燃料が供給されるため、燃料電池を積層した場合の電池特性および電池寿命が伸長させる作用がある。

自然循環供給方式と併用して補助装置を用いて連続的あるいは間欠的に作動させるため補填の消費電力も少なく、燃料消費量を軽減させると共に電池性能や信頼性を向上することが出来ることとなる。

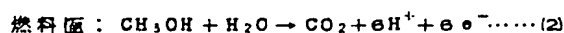
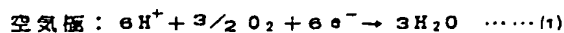
#### 実施例

以下に実施例によりさらに詳しく説明する。

#### 実施例1

アルコール燃料電池を構成する燃料極と空気極

料はその消費量に応じてアルコール燃料注液口13より補給される。空気極2は⊕端子14、燃料極3には⊖端子15が取り付けられている。つぎに第2図に示す様に空気極2の中には導電性多孔質基体(カーボンペーパー)16を介して撥水处理した白金触媒担持炭素材料からなり、燃料極3は撥水層17と触媒層18からなり、触媒層18には白金-ルテニウム触媒が担持された炭素材料からなり、陽イオン交換膜1側に密着している。燃料極3の撥水層17はアルコール燃料水溶液7側に配置されている。このような構成により、アルコール燃料電池の燃料極液室10と連通するアルコール燃料水溶液容器8内のアルコール燃料が両者間を矢印の方向に循環しながら、アルコール燃料とガス室6中の酸素(空気)が電気化学的反応をおこし、次の反応式に従って発電する事が出来る。本実施例ではアルコール燃料としてメタノールを用いた。



をその1例として特公昭63-115794号公報を参考にして製造した。その空気極と燃料極を陽イオン交換膜(デュボン社製ナフィオン膜)を介して使用したアルコール燃料電池の構成を第1図に示す。また、燃料極の拡大構成部分を第2図に示す。第1図において、陽イオン交換膜1を介して空気極2と燃料極3が配置され、酸化剤である空気は空気供給口4より入り、ガス室6を通過して、空気排出口8より排出される。一方、還元剤であるアルコール燃料は水と混合され、アルコール燃料水溶液7としてアルコール燃料水溶液容器8内に貯蔵され、アルコール燃料が反応して生成したガス(主に炭酸ガス)9は燃料極液室10内を上昇して、アルコール燃料水溶液7の排出口11より、アルコール燃料水溶液7と共に排出される。この反応生成ガス9が燃料極液室10内を上昇しやすい様に排出口11である先端開口部が排出液面12より上部に配置されている。この排出口より出て来たアルコール燃料水溶液は再びアルコール燃料水溶液容器8に還流される。アルコール燃



(2)、(3)式からわかるように、反応生成物である炭酸ガスが、燃料極13の撥水層17を通過して気泡状態9となってアルコール燃料水溶液7中に放出され、その気泡状態9の炭酸ガスが上昇する時、アルコール燃料も移動し、負荷に応じたアルコール燃料の循環が出来る。とくに比重の小さいアルコール燃料水溶液中であるから燃料極液室10内を均一な分布で、しかも大きな上昇速度で循環する事が出来る。

#### 実施例2

実施例1と同じ製法による空気極2と燃料極3を用い、両電極間に陽イオン交換膜1(デュボン社製ナフィオン膜)を介して構成したアルコール燃料電池の積層型構成の概念図を第3図に示す。また、積層電池の拡大構成部分を第4図に示す。第3図において、還元剤であるアルコール燃料を含むアルコール燃料水溶液7を貯蔵するアルコール燃料水溶液容器8が積層燃料電池本体19の各単電池燃料極液室10とアルコール燃料水溶液分

配口20と排出口11を介して連通し、反応生成ガス9の上昇作用によってアルコール燃料が各単電池燃料極液室10内を通過して循環しやすい様に各単電池の排出口11である先端開口部が排出液面12より上部に配置されている。この排出口11より出て来たアルコール燃料水溶液7は再びアルコール燃料水溶液容器8に還流される。アルコール燃料の消費量に応じて、アルコール燃料は注液口13より補給される。酸化剤である空気は燃料電池側面窓より供給され、反対側の側面窓及び上面窓より排出されるような構成とした。つぎに第4図に示すように左側から空気極2、陽イオン交換膜1、燃料極3、液室10、分離板21、ガス(空気)室5、空気極2、陽イオン交換膜1の順序に構成一体化されている。このような構成により、積層型アルコール燃料電池の各単電池燃料極液室10と連通するアルコール燃料水溶液容器8(例えばコ字型状の容器)内のアルコール燃料が両者間を矢印の方向に循環しながらアルコール燃料とガス室5中の空気(酸素)が電気化学的反

アルコール燃料電池を第6図に示す。第6図よりコ字型アルコール燃料水溶液容器8の下部付近で2分する容器間に直列にアルコール燃料水溶液供給装置25(液ポンプ)を配置したものである。この構成により、燃料極液室10内の反応生成ガスである気泡9の上昇作用と液ポンプ25の駆動によるアルコール燃料水溶液7の循環作用の併用によって、各単電池燃料極液室10内にアルコール燃料水溶液7を供給する構成と作動方法である。この構成及び作動方法以外はすべて実施例2と同じものである。

#### 実施例5

実施例1と同じ製法による空気極2と燃料極3を用い、両電極間に陽イオン交換膜1(デュボン社製ナフィオン膜)を介して構成した積層型アルコール燃料電池を第7図に示す。第7図よりコ字型アルコール燃料水溶液容器8の下部付近に2分する容器内にアルコール燃料水溶液流路26と並列に同供給装置であるアルコール燃料水溶液供給ポンプ25を配置したものである。

をおこし、負荷を連続的に取り出す事ができる。

#### 実施例3

実施例1と同じ製法による空気極2と燃料極3を用い、両電極間に陽イオン交換膜1(デュボン社製ナフィオン膜)を介して構成した積層型アルコール燃料電池を第5図に示す。第5図より積層型アルコール燃料電池の各単電池燃料極液室10内に気体供給装置(空気供給ポンプ)23の駆動によって気泡24を供給するため、燃料極液室10内に向って気泡供給口を有する分岐管22をコ字型アルコール燃料水溶液容器8の底部付近に設け、反応生成ガスである気泡9と併用して、各単電池燃料極液室10内にアルコール燃料水溶液7を供給する構成と作動方法である。この構成及び作動方法以外は、すべて実施例2と同じ構成によるものである。

#### 実施例4

実施例1と同じ製法による空気極2と燃料極3を用い、両電極間に陽イオン交換膜1(デュボン社製ナフィオン膜)を介して構成した積層型アル

この構成により燃料極液室10内の反応生成ガスである気泡9の上昇作用とアルコール燃料水溶液供給ポンプ25の駆動によるアルコール燃料水溶液7の循環作用の併用あるいは単独によって、各単電池燃料極液室10内にアルコール燃料水溶液7を供給する構成と作動方法である。

燃料電池から取り出す負荷が大きい場合はとくにアルコール燃料水溶液供給ポンプ25の駆動を併用し、アルコール燃料の供給量を増加させ、低負荷の時はアルコール燃料水溶液供給ポンプ25の駆動を停止し、負荷以外の消費電力を減少させる。アルコール燃料水溶液供給ポンプ25の代わりに、第8図に示すような羽根式回転駆動装置25'の様な装置でも同じ効果が得られる。この構成及び作動方法以外は、すべて実施例2と同じものである。

実施例2～5に関して図面に記載しているようなコ字型のアルコール燃料水溶液容器を用いているが、要はアルコール燃料電池の燃料極液室内をアルコール燃料が循環しやすい構造のものが好ま

しい。燃料電池燃料液室10内の下部から供給されるアルコール燃料の流路は燃料電池本体内であってもよい。即ち分岐状のアルコール燃料水溶液流通管であってもよい。

#### 比較例

比較例として従来型燃料電池を第9図に示す。第9図のa-a'断面を第10図に示す。第9図において、燃料電池本体27と隔壁28, 28'の間にアノライト流路29, 29'を設け、アノライトは電池枠30の底面部より矢印方向に流れ、アノライト排出孔31より排出され、排出孔31はアノライト液面32よりは高い位置に配置され、アルコール燃料は燃料供給路33, 33'より燃料電池液室内に供給される。アノライトは矢印の方向に循環されながら、燃料極にアルコール燃料が供給される構成となっている。

第10図において電池枠の中に液室34, 燃料極35, 陽イオン交換膜36, 空気極37よりなる構成のものである。燃料極は炭素粉末に白金触媒が担持された構成のものであり、空気極は白金

本発明の燃料電池を作動させる事により、実施例1～5において、各種電流における平均単電池電圧は電流密度30 mA/cm<sup>2</sup>: 0.55～0.57 V, 電流密度60 mA/cm<sup>2</sup>: 0.39～0.41 V, 電流密度100 mA/cm<sup>2</sup>: 0.33～0.365 Vであり、実施例1～5における電圧差は各々0.02 V, 0.03 V, 0.035 Vと徐々に大きくなっているが、大きな差は認められない。これに対して、比較例における従来の燃料電池では、電流密度30 mA/cm<sup>2</sup>: 0.01～0.03 V, 電流密度60 mA/cm<sup>2</sup>: 0.01～0.03 V, 電流密度100 mA/cm<sup>2</sup>: 0.03～0.065 V程本発明の燃料電池に比較して電圧が低くなっている。とくに高い電流密度になる程、その傾向が大きく表われている。実施例2の燃料電池と比較しても電流密度によって0.01～0.03 V程高い電圧を示している。この理由として電解液と水との比重差があるため、比重の小さい水の方が反応生成ガス(炭酸ガス)の浮力が見掛上大きく働くために、アルコール燃料の循環を早くするために、燃料極電位が向上し電池電圧に差が表われたもの

触媒を担持した炭素粉末と撥水剤が混合され、加圧一体化されたものである。

本実施例の構成及び作動方法によるアルコール燃料電池の特性を表1に示す。測定条件としてはメタノール濃度3Mの水溶液を用い、触媒層には1.5M硫酸を含浸させた。測定温度60℃, 空気電圧は理論値の5倍以上とした。比較例としてはメタノール濃度が3Mの3M濃度硫酸溶液(アノライト)を用い、他の条件はすべて実施例1～5と同じとした。各電流密度における端子電圧を実施例と従来例を比較した。

表 1

	30 mA/cm <sup>2</sup>	60 mA/cm <sup>2</sup>	100 mA/cm <sup>2</sup>
実施例 1	0.57 V	0.40 V	0.34 V
" 2	0.55 V	0.395 V	0.33 V
" 3	0.55 V	0.39 V	0.35 V
" 4	0.56 V	0.41 V	0.365 V
" 5	0.56 V	0.41 V	0.365 V
比較例	0.54 V	0.38 V	0.30 V

と考えられる。とくに高い電流密度になるとその傾向が強くなる。

本実施例の中でも単電池と積層電池を比較しても、アノライトの導電性よりはアルコール燃料水溶液の導電性の方が小さいために液短絡による電池電圧は非常にわずかである。この事は実施例1と実施例2を見ればよくわかる。したがって、積層する事による自己消費電力は非常に少なく、実用上大きな利点となる。下の積層型燃料電池において、低電流密度では大きな電圧差は認められないが、高電流密度になると、反応生成ガスのみの上昇作用だけでは、アルコール燃料の循環が不十分になって来る。即ち負荷に応じた燃料極へのアルコール燃料の供給が不足する。そこでこの現象を解消するために燃料極の液室8内に空気供給ポンプにより気泡を余分に供給するとアルコール燃料水溶液の循環を補助し、燃料電池電圧の向上が認められる。さらに、アルコール燃料水溶液供給ポンプでアルコール燃料水溶液の循環を補助的に行なうと高電流密度において燃料電池の電圧が向

上している。この様に空気供給ポンプやアルコール燃料水溶液供給ポンプなどで負荷に応じて補助的に用いる事によって燃料電池に損傷を与えることなく長寿命で、高性能な燃料電池を得る事が出来る。空気供給ポンプ、アルコール燃料水溶液供給ポンプの駆動を必要に応じて、連続的あるいは間欠的に行なわせ、補助装置の消費電流を減少させ、アルコール燃料電池システムの発電効率を上げることができる。

また、本発明の燃料電池はアルコール(メタノール)と水を循環させるだけであるために、仮に外部に漏液させても機器を損傷する事がないが、従来の燃料電池ではアノライトに硫酸水溶液を用いるために機器の損傷が大きく、腐食性の点からも本発明の燃料電池が優れる。

気体供給装置として本実施例では空気供給ポンプを用いたが、圧縮ガス、その他の気体発生装置であればいずれでも同じ効果が得られる。また、アルコール燃料水溶液供給装置としてアルコール燃料水溶液供給ポンプを用いたが、一般に用いら

れる液体供給装置であればよい。本実施例では酸化剤に空気を用いたが、酸素ガスを用いると経済性は下がるがさらに高性能化のアルコール燃料電池が得られる。

還元剤としてはメタノールを用いたが、エチルアルコールなど他のアルコール燃料を用いてもよいが、メタノールが最も特性が優れている。

酸化剤である空気は燃料電池の側面より供給し、反対の側面あるいは上面から排出する様な構成としたが、燃料電池の底面より供給し、上面から排出する様な構成でもよい。また、アルコール燃料水溶液の排出口である先端開口部が排出液面より上部に配置する事によって、燃料極液室内のアルコール燃料水溶液が反応生成ガスによってより効率よく循環しやすくなった。燃料極液室内で気泡がたまり、アルコール燃料の分布が不均一になる状態がなくなった。したがって、アルコール燃料が均一に供給されるために燃料電池の寿命も長くなり、信頼性も優れることとなる。

#### 発明の効果

である。

1 ……陽イオン交換膜、3 ……燃料極、7 ……アルコール燃料水溶液、8 ……アルコール燃料水溶液容器、9 ……反応生成ガス(気泡状態)、10 ……燃料極液室、11 ……排出口、12 ……排出液面、17 ……撥水層、18 ……触媒層、22 ……分岐管、23 ……空気供給ポンプ、24 ……空気供給ポンプで供給する気泡、25 ……アルコール燃料水溶液供給ポンプ、26 ……アルコール燃料水溶液流路。

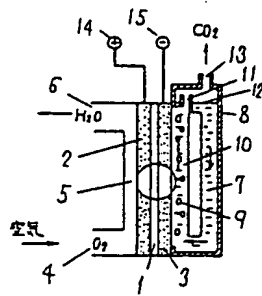
代理人の氏名 弁理士 栗野重孝ほか1名

以上の様に、本発明によればアルコール燃料水溶液を循環させるために安全性高く、高電流密度でも高い電圧を保持し、補機の消費電力も少なく、高効率で長時間発電しても電池性能の低下の少ないアルコール燃料電池及び作動方法を提供できるという効果が得られる。

#### 4. 図面の簡単な説明

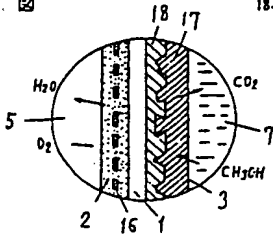
第1図はアルコール燃料電池の構成を示す図、第2図は第1図の燃料極の一部を拡大して示した図、第3図はアルコール燃料電池の積層構成を示す図、第4図は第3図の積層電池の一部を拡大して示した図、第5図は気体供給装置を備えた積層型アルコール燃料電池の構成を示す図、第6図はアルコール燃料水溶液供給ポンプを備えた積層型アルコール燃料電池の構成を示す図、第7図はアルコール燃料水溶液供給ポンプを流路と並列的に備えた積層型アルコール燃料電池の構成を示す図、第8図はアルコール燃料水溶液供給装置の他の例を示す図、第9図は従来のアルコール燃料電池の構成を示す図、第10図は第9図のa-a'断面図

第 1 図



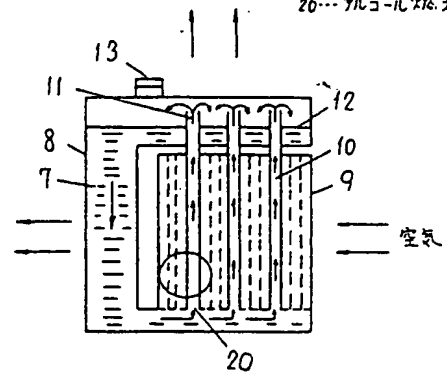
- 1... 陽イオン交換膜
- 2... 空気層
- 3... 燃料層
- 4... 空気供給口
- 5... ガス室
- 6... 空気排出口
- 7... アルコール燃料水溶液
- 8... アルコール燃料水溶液入口
- 9... 反応生成ガス
- 10... 燃料層液室
- 11... アルコール燃料水溶液排出口
- 12... 排液面
- 13... アルコール燃料水溶液口
- 14... 電極子
- 15... 電極子

第 2 図



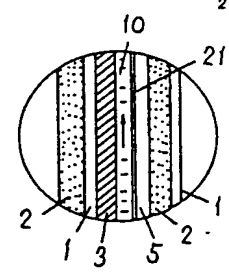
- 16... 多孔質基板
- 17... 排水層
- 18... 燃料層

第 3 図



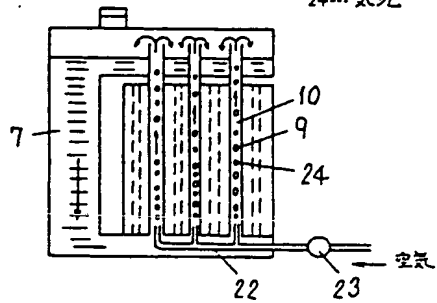
- 20... アルコール燃料水溶液分配口

第 4 図



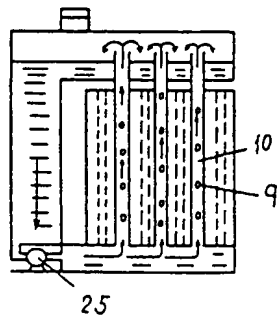
- 21... 隔壁板

第 5 図



- 22... 分岐管
- 23... 気体供給装置
- 24... 気室

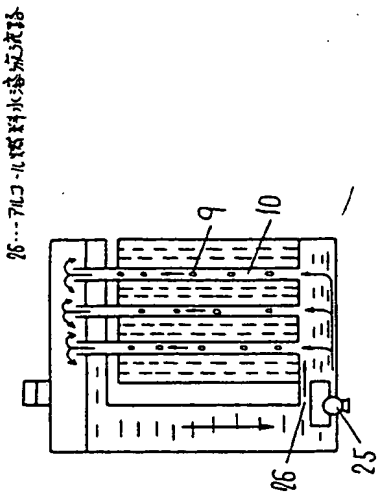
第 6 図



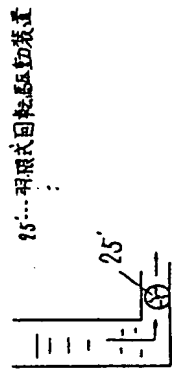
- 25... アルコール燃料水溶液供給装置



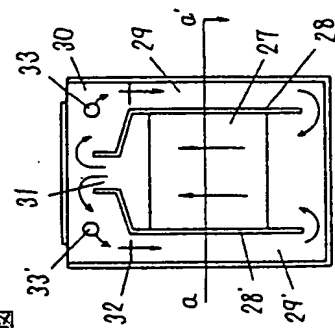
第 7 図



第 8 図



第 9 図



第 10 図

